

## FULL PAPER

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Platinum Complexes of 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dichalcogenoles

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Six platinum bisphosphine complexes, bearing dichalcogen acenaphthene ligands, have been prepared by metathesis from *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] (R<sub>3</sub> = Ph<sub>3</sub>, Ph<sub>2</sub>Me, PhMe<sub>2</sub>) and the dilithium salts of the parent 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dichalcogenoles [AcenapE<sub>2</sub>] (**L1** E = S, **L2** E = Se). For their synthesis, the appropriate disulfide or diselenide species was treated with super hydride [LiBEt<sub>3</sub>H] affording the dilithium salt by *in situ* reduction of the AcenapE<sub>2</sub> E-E bond. Further reaction, via metathetical addition to the *cis*-platinum precursor afforded the respective platinum(II) complex [Pt(5,6-AcenapE<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub>] (R<sub>3</sub> = Ph<sub>3</sub>: E = S **1**, Se **2**; R<sub>3</sub> = Ph<sub>2</sub>Me: E = S **3**, Se **4**; R<sub>3</sub> = PhMe<sub>2</sub>: E = S **5**, Se **6**).

All six complexes have been fully characterised, principally by multinuclear magnetic resonance spectroscopy, IR and MS. Selenium complexes **4** and **6** provide examples of AA'X spin systems, as displayed by their <sup>31</sup>P{<sup>1</sup>H} NMR spectra. X-ray structures were determined for **L1**, **L2**, **1**, **2**, **5** and **6** and analysed, where appropriate, by platinum metal geometry, *peri*-atom displacement, splay angle magnitude, acenaphthene ring torsion angles and E...E interactions. Platinum was found to adopt a distorted square-planar geometry in all four complexes, with the nature of the AcenapE<sub>2</sub> ligand playing little part in the conformation of the substituents bound to the trivalent phosphorus atoms.

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## Introduction

The coordination chemistry of *peri*-substituted naphthalenes and structurally related systems has been developed over the last 15 years.[1] Geometric constraints unique to these frameworks are imposed by a double substitution at the *peri*-positions (positions 1 and 8 of the naphthalene ring, 5 and 6 of acenaphthene),[2,3] placing large heteroatoms or groups in close proximity, usually within van der Waals radii.[4] A number of **investigators** have utilised this characteristic of the naphthalene scaffold to study bonding interactions in main group systems, where molecular geometry is determined by a competition between attractive (covalent and weak) forces and repulsive interactions (steric strain).[5,6] The distinguishing feature of *peri*-substitution is the ability to achieve a relaxed geometry via formation of a direct bond between the two *peri*-atoms.[7] Furthermore, proximity effects associated with *peri*-substitution favours complexation to a bridging metal species, providing the correct spacial arrangement for bidentate coordination.

Transition metal complexes incorporating 1,8-disubstituted naphthalene ligands have been well documented,[1] with the majority of examples reported bearing either bis(phosphine) or bis(thiolate) functionalities. Complexes assembled from ligands with Group 16 donor atoms invariably contain the naphthalene-1,8-dichalcogenole synthon, NapE<sub>2</sub>. [1] Initial investigations were

undertaken by the group of Teo, examining the extensive redox chemistry of tetrathionaphthalene (TTN), tetrachlorotetrathionaphthalene (TCTTN) and tetrathiotetracene (TTT) by preparing a series of singly and doubly bridged platinum and iridium complexes.[8] Further complexes bearing TTN type ligands were prepared coordinated to Fe, Co and Ni.[9] Similarly, oxidative addition of [Pd(PPh<sub>3</sub>)<sub>3</sub>] and [Pt(PPh<sub>3</sub>)<sub>4</sub>] to the related hexachloronaphthalene-1,8-dithiole (hcdtn) ligand affords two mononuclear square-planar complexes,[10,11] whilst treatment with RhCl(PPh<sub>3</sub>)<sub>3</sub> results in the formation of a five-coordinate Rh(III) complex.[11] In comparison, reaction of hcdtn with [Ni(cod)<sub>2</sub>] and PPh<sub>3</sub> affords a memorable trinuclear nickel(II) complex.[10]

During our investigations of *peri*-substituted naphthalenes, we prepared a series of platinum bisphosphine complexes bearing dichalcogen-derivatised naphthalene, acenaphthene and phenanthrene ligands via oxidative addition to zero-valent platinum species and from metathetical methods involving reaction with *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>].[12] In a comparative study, we reported a series of binuclear iridium(II) complexes, synthesised from the oxidative reactions of similar dithiole ligands with [{Ir(μ-Cl)(cod)}<sub>2</sub>].[13] To supplement our initial platinum study, [NapS<sub>2</sub>Pt(PPh<sub>3</sub>)<sub>2</sub>] was further treated with a range of Pt, Pd, Rh, Ir and Mo complexes to afford a series of bimetallic complexes containing an MM'S<sub>2</sub> core.[14] The corresponding reactions with [AuPPh<sub>3</sub>]ClO<sub>4</sub> and AgClO<sub>4</sub> afforded binuclear and tetranuclear gold clusters and tri- or tetranuclear silver clusters, the outcome dependent upon the stoichiometry of the reactants.[15] Further examples of multimetallic complexes bearing naphthalene dithiolate ligands have been reported in the literature, with examples of tetra- and pentanuclear copper(I) complexes of 1,8-naphthalene dithiolate[16] and oligomeric, dimeric and monomeric zinc complexes of 2,7-di-*tert*-butylnaphtho[1,8-*c,d*][1,2]dithiole and naphthoic anhydride

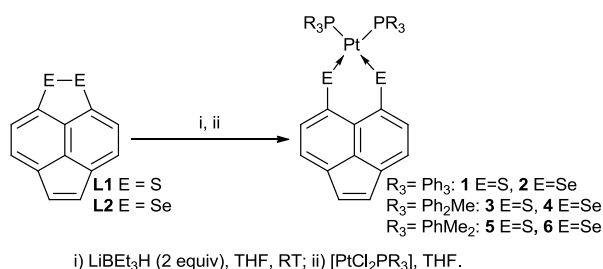
dithiole.[17] We have also prepared a series of titanocene complexes incorporating a range of dithioles with modified naphthalene-1,8-yl backbones, via oxidative addition reactions involving  $\text{TiCp}_2(\text{CO})_2$ . [18] A homologous series of three Group 4 metallocene complexes was also achieved from  $[\text{MCp}^*\text{Cl}_2]$  ( $\text{M} = \text{Ti, Zr, Hf}$ ). [19]

Whilst the coordination chemistry of sterically crowded 1,8-disubstituted naphthalenes has been well investigated, complexes formed from related *peri*-substituted 1,2-dihydroacenaphthylenes (acenaphthene)[3] have received much less attention. Our recent work has focused on the acenaphthene skeleton investigating chalcogen-tin compounds[20] and related halogen-chalcogen and chalcogen-chalcogen derivatives,[21] which were shown to be ideal building blocks for the construction of silver(I) coordination complexes and extended networks.[22] Here in we describe the preparation and structural analysis of six platinum bisphosphine complexes  $[\text{Pt}(5,6\text{-AcenapE}_2)(\text{PR}_3)_2]$  ( $\text{R}_3 = \text{Ph}_3$ ;  $\text{E} = \text{S}$  **1**, **2**;  $\text{R}_3 = \text{Ph}_2\text{Me}$ ;  $\text{E} = \text{S}$  **3**, **4**;  $\text{R}_3 = \text{PhMe}_2$ ;  $\text{E} = \text{S}$  **5**, **6**) formed by metathetical methods from 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dichalcogenoles [ $\text{AcenapE}_2$ ] (**L1**  $\text{E} = \text{S}$ , **L2**  $\text{E} = \text{Se}$ ) and *cis*- $[\text{PtCl}_2(\text{PR}_3)_2]$  ( $\text{R}_3 = \text{Ph}_3, \text{Ph}_2\text{Me}, \text{PhMe}_2$ ) (Scheme 1).

## Results and Discussion

Platinum **bisphosphine** complexes **1-6** bearing 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dichalcogenoles [ $\text{AcenapE}_2$ ] (**L1**  $\text{E} = \text{S}$ , **L2**  $\text{E} = \text{Se}$ ) have been prepared by metathesis from *cis*- $[\text{PtCl}_2(\text{PR}_3)_2]$  ( $\text{R}_3 = \text{Ph}_3, \text{Ph}_2\text{Me}, \text{PhMe}_2$ ) and the dilithium salts of the parent dichalcogen acenaphthene ligands (Scheme 1). All six complexes **1-6** and ligands **L1** and **L2** were synthesised and fully characterised, principally by multinuclear magnetic resonance and IR spectroscopy and mass spectrometry. The homogeneity of the new compounds was, where possible, confirmed by microanalysis.

5,6-Dihydroacenaphtho[5,6-*cd*]-1,2-dithiole ( $\text{AcenapS}_2$ ) **L1** and 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-diselenole ( $\text{AcenapSe}_2$ ) **L2** were prepared following standard literature procedures[23] starting from 5,6-dibromoacenaphthene.[24] Synthesis of the platinum metal complexes was based on previously well documented routes to complexes of 1,8-disubstituted naphthalene chalcogenides and related polyaromatic hydrocarbon compounds.[12] For their synthesis, the appropriate 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dichalcogenole was treated with two equivalents of super hydride  $[\text{LiBEt}_3\text{H}]$  in tetrahydrofuran, at room temperature, generating a reactive dilithium intermediate via *in situ* reduction of the E-E bond. Subsequent metathetical addition to the desired *cis*-platinum precursor afforded the respective platinum(II) complex  $[\text{Pt}(5,6\text{-AcenapE}_2)(\text{PR}_3)_2]$  ( $\text{R}_3 = \text{Ph}_3$ ;  $\text{E} = \text{S}$  **1**, **2**;  $\text{R}_3 = \text{Ph}_2\text{Me}$ ;  $\text{E} = \text{S}$  **3**, **4**;  $\text{R}_3 = \text{PhMe}_2$ ;  $\text{E} = \text{S}$  **5**, **6**) in good to moderate yields (43–76%; Scheme 1).



Scheme 1. Reaction scheme for the preparation of bisphosphine complexes  $[\text{Pt}(5,6\text{-AcenapE}_2)(\text{PR}_3)_2]$  **1-6** bearing 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dichalcogenoles **L1** and **L2**.

$^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopic data for the series of bisphosphine complexes is displayed in Table 1. The spectra of complexes **1**, **3** and **5**, bearing the sulfur ligand **L1**, display anticipated single resonances with platinum satellites, moving to lower chemical shifts as the alkyl group on phosphorus is varied from  $\text{R}_3 = \text{Ph}_3$  to  $\text{R}_3 = \text{PhMe}_2$  [**1**  $\delta = 23.52$  ppm,  $^1J(^{31}\text{P}, ^{195}\text{Pt}) = 2980$  Hz; **3**  $\delta = 4.51$  ppm,  $^1J(^{31}\text{P}, ^{195}\text{Pt}) = 2926$  Hz; **5**  $\delta = -13.14$  ppm  $^1J(^{31}\text{P}, ^{195}\text{Pt}) = 2861$  Hz]. A decrease in the coupling constants of the platinum satellites is also observed going from  $\text{Ph}_3$  to  $\text{PhMe}_2$ , consistent with the decrease in electronegativity of the alkyl substituents and an apparent decrease in the *s*-character of the bond.[25]

Table 1.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopic data for complexes **1-6**. [a]

	1	2	3	4	5	6
$^{31}\text{P}$ NMR	23.52	20.19	4.51	1.22	-13.14	-16.22
$^1J(^{31}\text{P}-^{195}\text{Pt})$	2980	3020	2926	2958	2861	2861
$^2J(^{31}\text{P}-^{77}\text{Se})$	-	-	-	-	-	47( <i>cis</i> );56( <i>trans</i> )

[a]  $\delta$  (ppm),  $J$  (Hz).

Platinum complexes **2**, **4** and **6**, containing two phosphine ligands and the symmetrical bis-selenium ligand **L2**, can be analysed as  $\text{AA}'\text{X}$  spin systems (disregarding satellites for  $^{31}\text{P}/^{77}\text{Se}$ - $^{195}\text{Pt}$  coupling; Figure 1).[26] The  $\text{AA}'$  nuclei correspond to the two  $^{31}\text{P}$  atoms which align with either a *cis* or *trans* configuration with respect to the low abundant  $^{77}\text{Se}$  NMR active isotope, the X-nucleus in the spin system (Figure 1). The presence of the NMR-inactive isotopomer of the X-nucleus at the second Se coordinating site thus breaks the symmetry of the molecule and ensures the two  $^{31}\text{P}$  environments are magnetically inequivalent. This secondary isotopomer effect, combined with the presence of weak  $^{31}\text{P}$ - $^{31}\text{P}$  coupling, creates a complex satellite system observed in both the  $^{31}\text{P}$  and  $^{77}\text{Se}$  NMR spectra of these compounds (Figure 1).

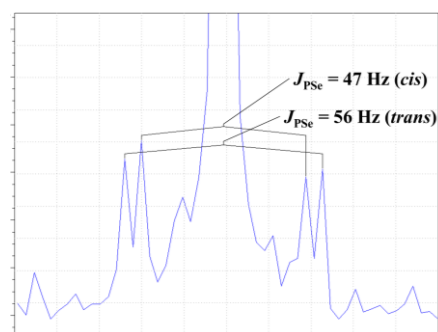


Figure 1. An expansion of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of complex **6** showing the satellites for *cis* and *trans*  $^2J(^{31}\text{P}, ^{77}\text{Se})$  coupling of an  $\text{AA}'\text{X}$  spin system (the satellites for the large  $^1J(^{31}\text{P}, ^{195}\text{Pt})$  coupling are omitted for clarity).

Difficulties obtaining data with sufficiently good enough signal-to-noise ratios resulted in the expected  $\text{AA}'\text{X}$  pattern not being fully resolved in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of complex **4**. Nevertheless, the standard single resonance (corresponding to molecules containing NMR-inactive Se nuclei) was observed, lying upfield with respect to the equivalent sulfur complex **3** and with expected satellites for  $^1J(^{31}\text{P}, ^{195}\text{Pt})$  coupling [**4**  $\delta = 1.22$  ppm,  $^1J(^{31}\text{P}, ^{195}\text{Pt}) = 2958$  Hz].

Table 2. Selected interatomic distances [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **L1**, **L2**, **1**, **2**, **5**, **6**

Compound	L1	L2	1	2	5	6
Ligand; <i>peri</i> -atoms	SS	SeSe	<b>L1</b> ; SS	<b>L2</b> , SeSe	<b>L1</b> ; SS	<b>L2</b> , SeSe
E(1)⋯E(9)	2.1025(19)	2.400(2) [2.380(2)]	3.267(4)	3.437(3)	3.273(7)	3.418(3)
$\Sigma r_{\text{vdW}} - \text{E}(1) \cdots \text{E}(9)^a$ ; % $\Sigma r_{\text{vdW}}$ [a]	1.498; 58	1.400; 63 [1.420; 63]	0.333; 91	0.363; 90	0.325; 91	0.381; 90
<i>Peri-region bond angles</i>						
E(1)-C(1)-C(10)	113.6(3)	114.0(9) [117.4(9)]	125.7(7)	127.2(12)	127.1(11)	131.0(10)
C(1)-C(10)-C(9)	120.2(5)	128.0(11) [122.6(11)]	128.9(8)	128.0(13)	128.7(12)	129.5(11)
E(9)-C(9)-C(10)	114.4(4)	114.9(9) [116.3(10)]	127.9(6)	130.5(10)	128.0(11)	125.9(10)
$\Sigma$ of bay angles	348.2(7)	356.9(17) [356.3(17)]	382.5(12)	385.7(20)	383.8(20)	386.4(18)
Splay angle <sup>b</sup>	-11.8	-3.1 [-3.7]	22.5	25.7	23.8	26.4
<i>Out-of-plane displacement</i>						
E(1)	0.022(1)	-0.053(1) [-0.061(1)]	0.170(1)	0.155(1)	0.044(1)	0.157(1)
E(9)	0.003(1)	-0.032(1) [0.023(1)]	0.075(1)	0.015(1)	0.127(1)	0.014(1)
<i>Central naphthalene ring torsion angles</i>						
C:(6)-(5)-(10)-(1)	179.84(1)	178.96(1) [177.76(1)]	177.98(1)	178.51(1)	179.37(1)	177.36(1)
C:(4)-(5)-(10)-(9)	179.55(1)	178.69(1) [177.07(1)]	-179.97(1)	178.25(1)	178.04(1)	173.18(1)

[a] van der Waals radii used for calculations:  $r_{\text{vdW}}(\text{S})$  1.80 $\text{\AA}$ ,  $r_{\text{vdW}}(\text{Se})$  1.90 $\text{\AA}$ [28] <sup>b</sup> Splay angle:  $\Sigma$  of the three bay region angles – 360.

In comparison, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of complexes **2** and **6** display the **expected** pattern for the AA' nuclei of an AA'X spin system.[26] In addition to the established single resonances accompanied by platinum satellites [**2**  $\delta$  = 20.19 ppm,  $^1J(^{31}\text{P},^{195}\text{Pt})$  = 3020 Hz; **6**  $\delta$  = -16.22 ppm,  $^1J(^{31}\text{P},^{195}\text{Pt})$  = 2861 Hz], satellites for  $^{77}\text{Se}$  coupling are also present in both spectra. In the spectrum of complex **6**, two sets of  $^{77}\text{Se}$  satellites are clearly present, with  $^2J(^{31}\text{P},^{77}\text{Se})$  values of 47 Hz and 56 Hz corresponding to the *cis* and *trans* couplings (Figure 1). Whilst it is impossible to assign the two distinct satellites as being either *trans* or *cis* to the  $^{77}\text{Se}$  nuclei in the system, the  $J$  values are consistent with those found in the naphthalene analogue [Pt(1,8- $\text{Se}_2$ -nap)(PMe<sub>3</sub>)<sub>2</sub>] (47 Hz and 53 Hz). In contrast, the  $^2J(^{31}\text{P},^{77}\text{Se})$  *cis/trans* coupling constants for complex **2** are of a similar magnitude, thus resulting in an overlap of the satellites in the  $^{31}\text{P}$  NMR spectrum, making exact values for the two couplings difficult to extract.  $^1J(^{31}\text{P}_\text{A},^{31}\text{P}_\text{A'})$  coupling constants are notoriously small for AA'X spin systems[27] and were not observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of complexes **2**, **4** and **6**. The partial solubility of the complexes also made obtaining  $^{77}\text{Se}$  NMR spectra with **reasonable** signal-to-noise ratios for these complexes problematic.

**X-ray investigations:** Crystals of **L1** and **L2** suitable for X-ray diffraction were obtained from hot hexane followed by cooling at -10 $^\circ\text{C}$  overnight. In addition, single crystals for complexes **1**, **2**, **5** and **6** were obtained by diffusion of hexane into saturated solutions of the individual compound in dichloromethane. Selenium ligand **L2** contains two nearly identical molecules in the asymmetric unit; all other compounds contain one molecule in the asymmetric unit. Selected interatomic distances, angles and torsion angles are listed in Tables 2 and 3. Further crystallographic information can be found in Table 4 and in the Electronic Supporting Information (ESI).

5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dichalcogenoles [AcenapE<sub>2</sub>] **L1** (E = S) and **L2** (E = Se) (Figure 2) unsurprisingly adopt similar molecular structures to naphthalene equivalents NapE<sub>2</sub>. [29] Nevertheless, introduction of the ethane linkage at the 1,2-positions in the acenaphthene molecules

naturally reduces the C4-C5-C6 bond angle (**L1/L2** 114 $^\circ$ /113 $^\circ$ ; cf. NapS<sub>2</sub>/NapSe<sub>2</sub> 125 $^\circ$ /123 $^\circ$ )[29] whilst simultaneously increasing the C1-C10-C9 angular splay (**L1/L2** 120 $^\circ$ /128 $^\circ$ ; cf. NapS<sub>2</sub>/NapSe<sub>2</sub> 118 $^\circ$ /122 $^\circ$ ),[29] consequently elongating the short S-S and Se-Se *peri*-bonds in these “simple” single bonded systems (**L1** 2.1025(19)  $\text{\AA}$ , cf. NapS<sub>2</sub> 2.0879(8)  $\text{\AA}$ ; **L2** 2.400(2)  $\text{\AA}$  [2.380(2)  $\text{\AA}$ , cf. NapSe<sub>2</sub> 2.3639(5)  $\text{\AA}$ ).[29] Steric demands imposed by the substitution of heavy chalcogen atoms are relieved in these systems by the formation of such strong E-E covalent bonds, regardless of the minor increase in their length. In the sulfur analogue **L1**, this is accompanied by a large negative splay angle as the exocyclic *peri*-bonds naturally converge (-11.8 $^\circ$  cf. NapS<sub>2</sub> -11.2 $^\circ$ ), and only a minor displacement of the sulfur atoms from the mean plane of the organic backbone, in line with the naphthalene compound (0.01-0.02  $\text{\AA}$ ).[29] Typical for systems incorporating larger substituents, the selenium counterpart **L2** exhibits a more positive splay angle (-3.1 $^\circ$  [-3.7 $^\circ$ ], cf. NapSe<sub>2</sub> -3.6 $^\circ$ )[29] with the two E-C<sub>Acenap</sub> bonds now adopting a more parallel alignment. Buckling of the two naturally planar carbon frameworks is minimal and comparable to the naphthalene compounds, with the greatest distortion observed in the selenium analogue **L2**; maximum C-C-C-C central acenaphthene torsion angles in the range 178-179 $^\circ$ .

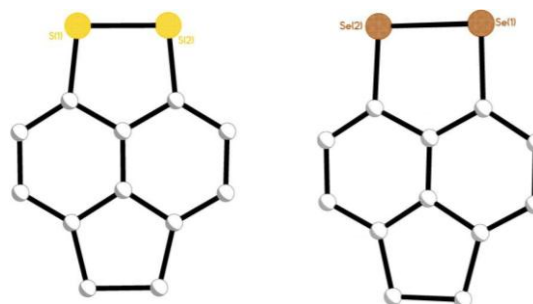


Figure 2. The molecular structures of 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dichalcogenoles [AcenapE<sub>2</sub>] (**L1** E = S, **L2** E = Se; H atoms omitted for clarity).

Table 3. Platinum coordination geometry; selected intramolecular distances [Å] and angles [°] for **1**, **2**, **5**, **6**

Complex	1	2	5	6
Ligand; <i>peri</i> -atoms	<b>L1</b> ; SS	<b>L2</b> , SeSe	<b>L1</b> ; SS	<b>L2</b> , SeSe
<i>Metal geometry – bond</i>				
E(1)-Pt(1)	2.336(2)	2.4558(16)	2.324(4)	2.449(3)
E(9)-Pt(1)	2.323(3)	2.4356(16)	2.324(5)	2.438(3)
P(1)-Pt(1)	2.301(2)	2.304(4)	2.258(5)	2.279(4)
P(2)-Pt(1)	2.295(2)	2.294(4)	2.267(4)	2.277(5)
<i>Metal geometry – bond angles</i>				
E(1)-Pt(1)-E(9)	89.07(8)	89.27(6)	89.61(15)	88.78(6)
E(1)-Pt(1)-P(1)	86.53(8)	86.47(10)	84.53(15)	86.60(11)
P(1)-Pt(1)-P(2)	97.51(8)	97.68(13)	100.84(15)	100.45(14)
E(9)-Pt(1)-P(2)	87.54(8)	87.56(10)	85.47(14)	84.67(11)
E(1)-Pt(1)-P(2)	172.20(9)	170.63(12)	173.00(16)	171.08(10)
E(9)-Pt(1)-P(1)	172.79(8)	171.95(11)	171.87(13)	173.09(12)
<i>Metal geometry – distortion</i>				
E <sub>2</sub> Pt-P(1) distance	0.229(1)	0.274(1)	0.220(1)	-0.204(1)
E <sub>2</sub> Pt-P(2) distance	-0.281(1)	-0.351(1)	-0.196(1)	0.240(1)
<i>Envelope geometry</i>				
E <sub>2</sub> C <sub>3</sub> -Pt angle	135.92(1)	139.16(1)	134.44(1)	133.77(1)
E <sub>2</sub> C <sub>3</sub> -Pt distance	1.152(1)	1.137(1)	1.175(1)	1.259(1)

Treatment of the dilithium salts of **L1** and **L2** with *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] afforded two isomorphous monomeric, mononuclear four coordinate platinum(II) complexes [Pt(5,6-AcenapE<sub>2</sub>)(Ph<sub>3</sub>)<sub>2</sub>] (**1** E = S; **2** E = Se; Figure 3). Similarly, the corresponding reactions with *cis*-[PtCl<sub>2</sub>(PPhMe<sub>2</sub>)<sub>2</sub>] generated a pair of equivalent isomorphous platinum(II) complexes [Pt(5,6-AcenapE<sub>2</sub>)(PhMe<sub>2</sub>)<sub>2</sub>] (**5** E = S; **6** E = Se; Figure 4). In each case, the symmetrical bidentate dichalcogen ligand binds via both E atoms forming a chelate ring with the central metal. The PtE<sub>2</sub>C<sub>3</sub> six-membered rings are hinged about the E...E vector and adopt a twisted envelope type conformation (Figure 5); E(1), E(9), C(1), C(10) and C(9) are essentially coplanar with the platinum atom lying in the *peri*-gap, displaced 1.15–1.26 Å above the E<sub>2</sub>C<sub>3</sub> plane, with the E(1)-Pt(1)-E(9) plane inclined by 134–139°.

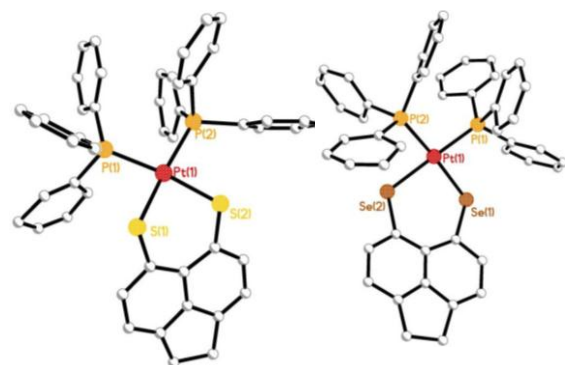


Figure 3. The molecular structures of complexes **1** and **2** formed from *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and bearing chalcogen ligands **L1** and **L2** (H atoms omitted for clarity).

As a consequence of the ligand geometry, the two phosphine moieties retain a *cis*-orientation around platinum and complete a

distorted square planar geometry. The P(1)-Pt(1)-P(2) angles for complexes **1** (97.51(8)°) and **2** (97.68(13)°) bearing the PPh<sub>3</sub> moiety show considerable deviation from the ideal 90° in accord with previously published examples. Counterintuitively, even larger angles are exhibited by complexes **5** (100.84(15)°) and **6** (100.45(14)°), despite incorporating the less sterically hindered PPhMe<sub>2</sub> functionality, associated with a smaller Tolman cone angle (PPhMe<sub>2</sub> 136° *cf.* PPh<sub>3</sub> 145°).[30] In contrast, corresponding E(1)-Pt(1)-E(9) angles are consistent in all four complexes with angles in the range 88.78(6)–89.61(15)°. The *cis* E(1)-Pt(1)-P(1), E(9)-Pt(1)-P(2) 84.53(15)–87.56(10)° and *trans* E(1)-Pt(1)-P(2), E(9)-Pt(1)-P(1) 170.63(12)–173.09(12)° angles also fall within accepted ranges for similar platinum complexes[12,27] but highlight the distortion of the square planar environment at the central platinum core. Pt-S (2.323(3)–2.336(2) Å), Pt-Se (2.436(2)–2.456(2) Å) and Pt-P (2.258(5)–2.304(4) Å) bond lengths correspond to distances seen in previous naphthalene complexes.[12,27] In addition to the in-plane deviations, further distortion is observed in all four complexes, with out-of-plane displacement of the coordinating E and P atoms reducing the planarity of the platinum primary coordination sphere. This can be compared by monitoring the location of the P atoms with respect to the mean E-Pt-E plane (Figure 6). In each case E(1), Pt(1) and E(9) are essentially coplanar with the P atoms displaced to opposite sides of this plane by 0.2–0.4 Å (Figure 6). The C-E-Pt bond angles are found to decrease from PPh<sub>3</sub> to PPhMe<sub>2</sub>, with average angles for **1** and **2** 111° compared with 109° in **5** and **6**. The reduction in the C-E-Pt angle is consistent with the smaller functionality on the phosphorus, allowing platinum to lie closer to the acenaphthene framework.

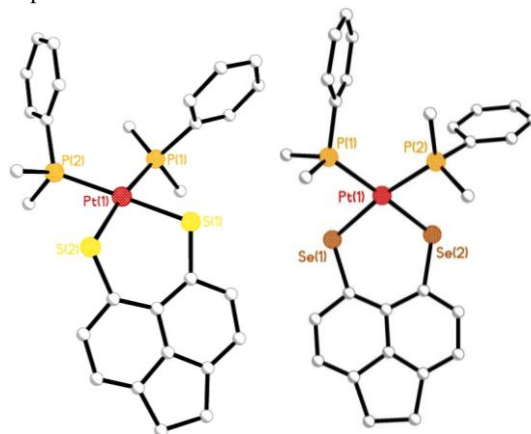


Figure 4. The molecular structures of complexes **5** and **6** formed from *cis*-[PtCl<sub>2</sub>(PPhMe<sub>2</sub>)<sub>2</sub>] (H atoms omitted for clarity).

The arrangement of substituents in trivalent phosphorus ligands is dictated by steric effects; R-P-R' angles are commonly less than 109.5°, approaching an ideal tetrahedral geometry as bulky groups are added.[30] In complexes **1**, **2**, **5** and **6** the nature of the AcenapE<sub>2</sub> ligand has no apparent effect on the conformation of the phosphorus moiety, with comparable R-P-R angles for **1** (av. 103.5°) and **2** (av. 103.7°), **5** (av. 102.3°) and **6** (av. 102.8°) respectively. Whilst the average of the C<sub>Ph</sub>-P-C<sub>Ph</sub> angles in **1** and **2** (av. 104°) is closer to that of a standard tetrahedral arrangement (as expected for larger substituents),[30] the angles range between 97.6(4)° and an unusually large 111.8(4)° (*cf.* **5/6** 99.6(6)–105.8(8)°). As might be expected from the larger steric influence of the PPh<sub>3</sub> group compared with PPhMe<sub>2</sub>, longer Pt-P bonds are observed in **1** and **2** (av. 2.30 Å) compared with **5** and **6** (2.27 Å). Whilst



steric effects dominate the configuration of substituents around phosphorus, weak interactions between the functional groups of neighbouring phosphorus atoms can influence the structure of the complex. In complexes **1** and **2**, two neighbouring phenyl rings attached to independent P atoms adopt a parallel alignment similar to the face-to-face offset arrangement (Figure 7),[31] with non-bonded distances between interacting centroids (cg(25-30)⋯cg(31-36): **1** 3.765(1)Å; **2** 3.764(1)Å) within the range for typical  $\pi\cdots\pi$  stacking (3.3-3.8 Å).[31] Similarly, complexes **5** and **6** exhibit weak CH⋯ $\pi$  type non-conventional hydrogen bond interactions[32] between neighbouring methyl and phenyl moieties of adjacent phosphorus groups (**5** C(14)-H(14C)⋯cg(23-28) 2.61 Å; **6** C(21)-H(21A)⋯cg(15-20) 2.72 Å; Figure 8).

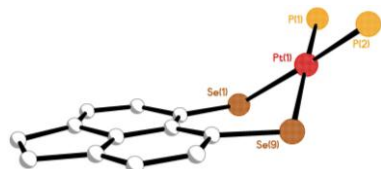


Figure 5. The open envelope configuration of the 6-membered chelate ring, formed from bidentate Se coordination of **L2** in complex **6** (phenyl and methyl groups and H atoms omitted for clarity).

Unsurprisingly, cleavage of the short E-E covalent bond and subsequent coordination to platinum in complexes **1**, **2**, **5** and **6** causes steric strain to accumulate between the bulky chalcogen atoms. Repulsive interactions between the two *peri*-functionalities, resulting from sub-van der Waals contacts, leads to deformation of the carbon framework via in-plane and out-of-plane distortions and buckling of the aromatic ring system (angular strain), ultimately disrupting the relaxed geometry previously achieved by the free ligands. As a consequence of the square planar metal geometry, the exocyclic E-C<sub>Acenap</sub> bonds now diverge, resulting in large positive splay angles in the range 23-26° and extended non-bonded E⋯E distances, greater than 1 Å longer than the E-E distances in the AcenapE<sub>2</sub> ligands (**1** 3.267(4) Å, **5** 3.273(7) Å; cf. **L1** 2.1025(19) Å; **2** 3.437(3) Å, **6** 3.418(3) Å; cf. **L2** 2.400(2) Å). This is accompanied by an increase in the out-of-plane displacement of the *peri*-atoms (0-0.2 Å; cf. **L1/L2** 0-0.05 Å) and a reduction in the planarity of the carbon skeleton (C-C-C-C torsion angles 0.1-7°; cf. **L1/L2** 0-0.1°). As can be seen from the magnitude of the E⋯E *peri*-separations, the subtle change of the phosphorus functionality from PPh<sub>3</sub> to PPhMe<sub>2</sub> has only a minor effect on the geometry of the acenaphthene fragment in these complexes. The most notable difference is observed within the bay-region, with marginally larger splay angles exhibited by complexes **2** and **6** (PPhMe<sub>2</sub>), increasing by ~1° compared with **1** and **5** (PPh<sub>3</sub>). Naturally, selenium analogues **2** and **6** exhibit greater molecular distortion within the acenaphthene fragment and longer *peri* E⋯E distances compared with sulfur equivalents **1** and **5**, in line with the greater bulk of the interacting atoms.



Figure 6. Out-of-plane distortion of the square planar geometry in **5** and **6**; displacement of the P atoms from the mean E-Pt-E plane (phenyl and methyl groups and H atoms omitted for clarity).

During an earlier study of platinum bisphosphine complexes bearing a range of dichalcogen derivatised naphthalene, acenaphthene and phenanthrene ligands, we prepared [Pt(1,8-NapSe<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] **N2**, the naphthalene analogue of complex **2**. [12] Although both compounds adopt comparable structures in the solid, introduction of the ethane linkage at the 1,2-positions of complex **2** has a noticeable influence on the phosphorus geometry and degree of molecular distortion in the organic backbone compared with **N2**. The greatest discrepancy between the two compounds is found in the planarity of the organic frameworks, with significantly less buckling observed within the acenaphthene ring system of **2** (maximum C-C-C-C central ring torsion angles ~2°; cf. **N2** ~1-5°).[12] Associated with this is a reduction in out-of-plane distortion, where one of the selenium atoms in **2** essentially resides on the mean acenaphthene plane, with the second atom displaced by only ~0.1 Å (cf. **N2** both Se atoms displaced ~0.2 Å from the mean naphthalene plane).[12] The natural splay of the exocyclic bonds in acenaphthene compounds compared with naphthalene equivalents accounts for the larger in-plane distortion observed in **2** (splay angle: 25.7°; cf. **N2** 23.8° [20.0°]), resulting in a minor lengthening of the Se⋯Se separation (**2** 3.437(3) Å; **N2** 3.37(1) Å [3.36(1) Å]).[12]

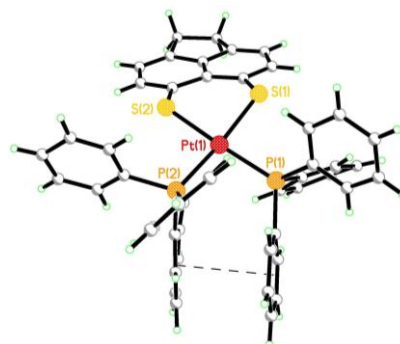


Figure 7. Overlapping phenyl rings in the isomorphous complexes **1** (shown) and **2** align with a weak face-to-face offset arrangement and interact via weak  $\pi\cdots\pi$  stacking.

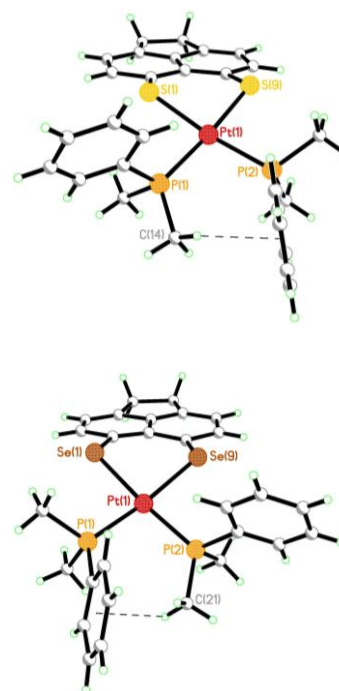


Figure 8. Adjacent phenyl and methyl moieties interact in **5** and **6** via weak non-conventional CH⋯ $\pi$  type interactions.

**Table 4.** Crystallographic data for **L1, L2, 1, 2, 5, 6**

Compound	L1	L2	1	2	5	6
Empirical Formula	C <sub>12</sub> H <sub>8</sub> S <sub>2</sub>	C <sub>12</sub> H <sub>8</sub> Se <sub>2</sub>	C <sub>48</sub> H <sub>38</sub> P <sub>2</sub> PtS <sub>2</sub>	C <sub>48</sub> H <sub>38</sub> P <sub>2</sub> PtSe <sub>2</sub>	C <sub>28</sub> H <sub>30</sub> P <sub>2</sub> PtS <sub>2</sub>	C <sub>28</sub> H <sub>30</sub> P <sub>2</sub> PtSe <sub>2</sub>
Formula Weight	216.32	310.12	935.99	1029.79	687.70	781.50
Temperature (°C)	-148(1)	-148(1)	-180(1)	-180(1)	-148(1)	-148(1)
Crystal Colour, Habit	orange, platelet	green, platelet	orange, prism	orange, prism	orange, platelet	orange, plate
Crystal Dimensions (mm <sup>3</sup> )	0.09 X 0.09 X 0.03	0.30 X 0.30 X 0.02	0.20 X 0.20 X 0.20	0.10 X 0.10 X 0.03	0.17 X 0.08 X 0.02	0.15 X 0.15 X 0.09
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Lattice Parameters	a = 13.871(8) Å b = 4.952(3) Å c = 14.633(7) Å - β = 116.097(12)° -	a = 7.359(5) Å b = 21.383(14) Å c = 12.304(9) Å - β = 99.016(19)° -	a = 9.769(3) Å b = 17.571(5) Å c = 22.605(6) Å - β = 102.379(7)° -	a = 9.797(4) Å b = 17.656(5) Å c = 22.821(8) Å - β = 101.690(8)° -	a = 9.978(3) Å b = 11.416(4) Å c = 11.731(4) Å α = 106.918(9)° β = 92.914(10)° γ = 95.035(9)°	a = 10.111(7) Å b = 11.637(11) Å c = 11.678(10) Å α = 106.30(3)° β = 94.62(2)° γ = 93.48(3)°
Volume (Å <sup>3</sup> )	V = 902.7(8)	V = 1912(2)	V = 3790(2)	V = 3865(3)	V = 1269.4(7)	V = 1310(2)
Space Group	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n	P-1	P-1
Z value	4	8	4	4	2	2
Dcalc (g/cm <sup>3</sup> )	1.592	2.154	1.640	1.769	1.799	1.982
F000	448	1184	1864	2008	676	748
m(MoKa) (cm <sup>-1</sup> )	5.346	76.842	39.177	56.169	58.114	82.538
No. of Reflections Measured	7383	15458	23502	24021	8862	11373
Rint	0.0660	0.1143	0.1206	0.1944	0.0909	0.0604
Min and Max Transmissions	0.765 - 0.984	0.442 - 0.858	0.201 - 0.457	0.306 - 0.845	-	0.271 - 0.476
Observed Reflection (No. Variables )	2055(127)	3850(253)	6898(466)	7007(459)	4268(298)	5707(298)
Reflection/Parameter Ratio	16.18	15.22	14.80	15.27	14.32	19.15
Residuals: R <sub>1</sub> (I>2.00σ(I))	0.0904	0.0981	0.0701	0.0898	0.0771	0.0611
Residuals: R (All reflections)	0.1297	0.1337	0.0884	0.1314	0.0918	0.0911
Residuals: wR <sub>2</sub> (All reflections)	0.2913	0.2569	0.1938	0.2369	0.1529	0.2645
Goodness of Fit Indicator	1.133	1.240	1.069	1.052	1.193	1.039
Maximum peak in Final Diff. Map	1.63 e <sup>-</sup> /Å <sup>3</sup>	1.40 e <sup>-</sup> /Å <sup>3</sup>	2.06 e <sup>-</sup> /Å <sup>3</sup>	1.83 e <sup>-</sup> /Å <sup>3</sup>	1.57 e <sup>-</sup> /Å <sup>3</sup>	2.28 e <sup>-</sup> /Å <sup>3</sup>
Minimum peak in Final Diff. Map	-1.01 e <sup>-</sup> /Å <sup>3</sup>	-1.85 e <sup>-</sup> /Å <sup>3</sup>	-3.40 e <sup>-</sup> /Å <sup>3</sup>	-2.24 e <sup>-</sup> /Å <sup>3</sup>	-2.97 e <sup>-</sup> /Å <sup>3</sup>	-4.62 e <sup>-</sup> /Å <sup>3</sup>

Whilst the in-plane Se-Pt-Se (86-89°), Se-Pt-P (86-89°) and P-Pt-P (98-99°) angles are comparable in both complexes, out-of-plane displacement (metal geometry) of the two P atoms with respect to the Se<sub>2</sub>Pt plane is marginally greater in the naphthalene analogue (~0.4-0.5 Å; *cf.* **2** 0.2-0.3 Å).[12] As might be expected, the PPh<sub>3</sub> groups in **2** adopt a similar configuration to those found in the naphthalene analogue, with comparable R-P-R angles for the two complexes (98-113°). Interestingly, whilst neighbouring phenyl rings of complex **N2** overlap, the distance between the two interacting centroids (4.167(1) Å [4.166(1) Å]) is **outside** the range for standard  $\pi \cdots \pi$  stacking to occur (3.3-3.8 Å).[12,31]

## Conclusions

The work presented in this paper builds on our previous studies of platinum bisphosphine complexes bearing dichalcogenide based ligands.[12] Herein we present the synthesis of a related series of platinum complexes **1-6** incorporating 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dichalcogenoles [AcenapE<sub>2</sub>] **L1** (E = S) and **L2** (E = Se) and *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] (R<sub>3</sub> = Ph<sub>3</sub>, Ph<sub>2</sub>Me, PhMe<sub>2</sub>). For their synthesis, the appropriate disulfide or diselenide species was treated with super hydride [LiBEt<sub>3</sub>H] affording the dilithium salt by *in situ* reduction of the AcenapE<sub>2</sub> E-E bond. Further reaction, via

metathetical addition to the *cis*-platinum precursor afforded the respective platinum(II) complex [Pt(5,6-AcenapE<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub>] (R<sub>3</sub> = Ph<sub>3</sub>; E = S **1**, Se **2**; R<sub>3</sub> = Ph<sub>2</sub>Me; E = S **3**, Se **4**; R<sub>3</sub> = PhMe<sub>2</sub>; E = S **5**, Se **6**). Sulfur complexes **1**, **3** and **5** display expected single resonances with platinum satellites in their respective <sup>31</sup>P{<sup>1</sup>H} NMR spectra, moving to lower chemical shifts and with decreasing <sup>1</sup>J(<sup>31</sup>P, <sup>195</sup>Pt) coupling constants as the alkyl group on phosphorus is varied from R<sub>3</sub> = Ph<sub>3</sub> to R<sub>3</sub> = PhMe<sub>2</sub>. The inclusion of the low abundant <sup>77</sup>Se NMR active isotope in complexes **2**, **4** and **6** provides extra complexity to their respective <sup>31</sup>P{<sup>1</sup>H} NMR spectra. These can be analysed as AA'X if the satellites for <sup>31</sup>P/<sup>77</sup>Se-<sup>195</sup>Pt coupling are disregarded.[26] The AA' nuclei correspond to the two <sup>31</sup>P atoms which align with either a *cis* or *trans* configuration with respect to the X-nucleus in the spin system (the <sup>77</sup>Se NMR active isotope), making them magnetically inequivalent. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of complex **6** displays the **expected** pattern for the AA' nuclei of an AA'X spin system;[26] in addition to the established single resonance accompanied by satellites for <sup>1</sup>J(<sup>31</sup>P, <sup>195</sup>Pt) coupling, two sets of <sup>77</sup>Se satellites are clearly present, with <sup>2</sup>J(<sup>31</sup>P, <sup>77</sup>Se) values of 47 Hz and 56 Hz corresponding to the *cis* and *trans* couplings. <sup>1</sup>J(<sup>31</sup>P<sub>A</sub>, <sup>31</sup>P<sub>A</sub>) coupling constants are notoriously small for AA'X spin systems and were not observed in the spectra of **2**, **4** and **6**.[27]

X-ray structures determined for **1**, **2**, **5** and **6** were analysed by platinum metal geometry, *peri*-atom displacement, splay angle magnitude, acenaphthene ring torsion angles and E...E

interactions and compared to the structures of the free ligands **L1** and **L2**. In each complex the symmetrical bidentate AcenapE<sub>2</sub> ligand coordinates to platinum to form a six-membered chelate ring which adopts a twisted envelope type motif. The two phosphine ligands retain a *cis*-orientation around platinum which lies at the centre of a distorted square-planar environment. Naturally, coordination to platinum and cleavage of the E-E bond results in a dramatic increase in molecular distortion in the acenaphthene component of **1**, **2**, **5** and **6** compared with free ligands **L1** and **L2**. Divergence of the exocyclic bonds results in large positive splay angles in the range 23-26° and extended non-bonded E...E distances, 1 Å longer than the E-E distances in the AcenapE<sub>2</sub> ligands. The nature of the AcenapE<sub>2</sub> ligand has no apparent effect on the conformation of the phosphorus moiety, with comparable R-P-R angles for **1** and **2**, **5** and **6** respectively. Similarly, the subtle change of the phosphorus functionality from PPh<sub>3</sub> to PPhMe<sub>2</sub> has only a minor effect on the geometry of the acenaphthene fragment in these complexes.

## Experimental Section

All experiments were carried out under an oxygen- and moisture-free nitrogen atmosphere using standard Schlenk techniques and glassware. Reagents were obtained from commercial sources and used as received. Dry solvents were collected from a MBraun solvent system. Elemental analyses were performed by Stephen Boyer at the London Metropolitan University. Infra-red spectra were recorded as KBr discs in the range 4000-300 cm<sup>-1</sup> on a Perkin-Elmer System 2000 Fourier transform spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ(H) and δ(C) referenced to external tetramethylsilane. <sup>31</sup>P and <sup>77</sup>Se NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ(P) and δ(Se) referenced to external phosphoric acid and dimethylselenide respectively. Assignments of <sup>13</sup>C and <sup>1</sup>H NMR spectra were made with the help of H-H COSY and HSQC experiments. All measurements were performed at 25 °C. All values reported for NMR spectroscopy are in parts per million (ppm). Coupling constants (*J*) are given in Hertz (Hz). Mass spectrometry was performed by the University of St. Andrews Mass Spectrometry Service; Electrospray Mass Spectrometry (ESMS) was carried out on a Micromass LCT orthogonal accelerator time of flight mass spectrometer. Platinum metal precursors *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)] (R<sub>3</sub> = Ph<sub>3</sub>, Ph<sub>2</sub>Me, PhMe<sub>2</sub>) were prepared following standard literature procedures.[12]

**5,6-dihydroacenaphtho[5,6-*cd*][1,2]dithiole [AcenapS<sub>2</sub>] (**L1**):** The title compound was prepared by a method previously described.[23] To a stirred solution of 5,6-dibromoacenaphthene (5.0 g, 16.03 mmol) and TMEDA (4.8 mL, 16.03 mmol) in diethyl ether (200 mL) was slowly added a 2.5 M hexane solution of *n*-butyllithium (6.4 mL, 16.03 mmol) at -78°C. After the mixture was stirred for 15 min at this temperature, sulfur flowers (0.51 g, 16.03 mmol) were added and stirring was continued at -40 °C for 2 h. The mixture was cooled again to -78°C, after which a 2.5 M hexane solution of *n*-butyllithium (6.4 mL, 16.03 mmol) was added and the reaction mixture stirred at this temperature for 15 min. Additional sulfur (0.51 g, 16.03 mmol) was added and the reaction mixture stirred for a further 2 h at -40 °C. The mixture was then quenched with acetic acid (2 mL) and exposed to an air stream overnight for oxidation. The resulting solution was concentrated under reduced pressure and after water was added, the mixture was extracted with dichloromethane. The extract was dried over anhydrous magnesium sulfate. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (hexane). An analytically pure sample was obtained by recrystallization from hexane

to give the desired product as orange crystals (0.70 g, 20%); mp 178-182 °C; (Found: C, 66.5; H, 3.8. *Anal. Calc.* for C<sub>12</sub>H<sub>8</sub>S<sub>2</sub>: C, 66.6; H, 3.7%); δ<sub>H</sub>(270 MHz, CDCl<sub>3</sub>, 25 °C, Me<sub>4</sub>Si) 7.06 (1 H, d, <sup>3</sup>J<sub>HH</sub> 7.5, Acenap 4,7-H), 7.02 (1 H, d, <sup>3</sup>J<sub>HH</sub> 7.2, Acenap 3,8-H), 3.29 (4 H, s, 2 x CH<sub>2</sub>); δ<sub>C</sub>(67.9 MHz; CDCl<sub>3</sub>; 25 °C; Me<sub>4</sub>Si) 121.1(s), 116.9(s), 30.7(s,CH<sub>2</sub>); *m/z* (ES<sup>+</sup>) 215.87 ([M]<sup>+</sup>, 100%).

**5,6-dihydroacenaphtho[5,6-*cd*][1,2]diselenole [AcenapSe<sub>2</sub>] (**L2**):** The title compound was prepared by a method previously described.[23] To a stirred solution of 5,6-dibromoacenaphthene (2.62 g, 8.40 mmol) and TMEDA (2.5 mL, 16.1 mmol) in diethyl ether (200 mL) was slowly added a 2.5 M hexane solution of *n*-butyllithium (3.4 mL, 8.40 mmol) at -78°C. After the mixture was stirred for 15 min at this temperature, selenium powder (0.66 g, 8.40 mmol) was added and stirring was continued at -40 °C for 2 h. The mixture was cooled again to -78°C, after which a 2.5 M hexane solution of *n*-butyllithium (3.4 mL, 8.40 mmol) was added and the reaction mixture stirred at this temperature for 15 min. Additional selenium powder (0.66 g, 8.40 mmol) was added and the reaction mixture stirred for a further 2 h at -40 °C. The mixture was then quenched with acetic acid (2 mL) and exposed to an air stream overnight for oxidation. The resulting solution was concentrated under reduced pressure and after water was added, the mixture was extracted with dichloromethane. The extract was dried over anhydrous magnesium sulfate. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (hexane/dichloromethane). An analytically pure sample was obtained by recrystallization from boiling toluene to give the desired product as green crystals (0.83 g, 32%); mp 198-200 °C; (Found: C, 46.5; H, 2.6. *Anal. Calc.* for C<sub>12</sub>H<sub>8</sub>Se<sub>2</sub>: C, 46.5; H, 2.6%); δ<sub>H</sub>(270 MHz, CDCl<sub>3</sub>, 25 °C, Me<sub>4</sub>Si) 7.21 (1 H, d, <sup>3</sup>J<sub>HH</sub> 7.4 Hz, Acenap 4,7-H), 7.05 (1 H, d, <sup>3</sup>J<sub>HH</sub> 7.2 Hz, Acenap 3,8-H), 3.26 (4 H, s, 2 x CH<sub>2</sub>); δ<sub>C</sub>(67.9 MHz; CDCl<sub>3</sub>; 25 °C; Me<sub>4</sub>Si) 121.7(s), 121.2(s), 30.4(s, Acenap CH<sub>2</sub>); δ<sub>Se</sub>(51.5 MHz; CDCl<sub>3</sub>; 25 °C; Me<sub>2</sub>Se) 424(s); *m/z* (ES<sup>+</sup>) 311.90([M+H]<sup>+</sup>, 100%), 309.91 ([M]<sup>+</sup>, 70%).

**[Pt(PPh<sub>3</sub>)<sub>2</sub>L1] (**1**):** Super Hydride (1.1 mL of a 1.0 M solution in THF, 1.1 mmol) was added in one portion to a solution of 5,6-dihydroacenaphtho[5,6-*cd*][1,2]dithiole (AcenapS<sub>2</sub>) **L1** (0.12 g, 0.56 mmol) in THF (20 mL). A colour change from bright red to pale yellow was observed, along with a small evolution of gas. The solution was transferred using a syringe to a suspension of *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.45 g, 0.56 mmol) in THF (10 mL) and stirred for 2 days giving a yellow solution. The mixture was filtered through a silica pad and eluted with dichloromethane (100 mL). The filtrate was evaporated to dryness under reduced pressure and re-dissolved in a minimum amount of dichloromethane (~10 mL). Diethyl ether (25 mL) and hexane (50 mL) were added slowly to induce precipitation. The resulting micro-crystalline solid was collected by filtration and washed with diethyl ether to yield the product as a light orange powder (0.4 g, 74%); mp 282-284 °C; (Found: C, 61.4; H, 4.0. *Anal. Calc.* for C<sub>48</sub>H<sub>38</sub>P<sub>2</sub>PtS<sub>2</sub>: C, 61.6; H, 4.1%); δ<sub>H</sub>(400 MHz, CDCl<sub>3</sub>, 25 °C, Me<sub>4</sub>Si) 7.48-7.38 (12 H, m, *PPh* 12,16-H), 7.34-7.26 (6 H, m, *PPh* 14-H), 7.27 (2 H, d, <sup>3</sup>J<sub>HH</sub> 7.3, Acenap 4,7-H), 7.14 (12 H, td, <sup>3</sup>J<sub>HH</sub> 7.7, <sup>4</sup>J<sub>HH</sub> 1.8, *PPh* 13,18-H), 6.90 (2 H, d, <sup>3</sup>J<sub>HH</sub> 7.3, Acenap 3,8-H), 3.17 (4 H, s, Acenap-CH<sub>2</sub>); δ<sub>C</sub>(75 MHz, CDCl<sub>3</sub>, 25 °C, Me<sub>4</sub>Si) 142.0(s), 140.7(s), 135.4-134.8 (m), 130.4 (s), 128.6-127.4 (m), 119.7(s), 30.9(s,CH<sub>2</sub>); δ<sub>P</sub>(109 MHz, CDCl<sub>3</sub>, 25 °C, H<sub>3</sub>PO<sub>4</sub>) 23.5 (*J*<sub>PP</sub> 2980); *m/z* (ES<sup>+</sup>) 826.66 ([M-SPh]<sup>+</sup>, 100%).

**[Pt(PPh<sub>3</sub>)<sub>2</sub>L2] (**2**):** Complex **2** was prepared following a similar procedure described for **1** but with Super Hydride (1.1 mL, 1.1 mmol), **L2** (0.18 g, 0.56 mmol) and *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.45 g, 0.56 mmol). The resulting solid was filtered off and washed with toluene (5 mL) and diethyl ether (2x10 mL) and dried *in vacuo* to yield an orange powder

(0.3 g, 54%); mp 185–186 °C; (Found: C, 55.9; H, 3.8. *Anal. Calc.* for  $C_{48}H_{34}PtP_2Se_2$ : C, 56.0; H, 3.7%);  $\delta_H$ (400 MHz,  $CDCl_3$ , 25 °C,  $Me_4Si$ ) 7.51 (2 H, d,  $^3J_{HH}$  7.28, Acenap 4,7-H), 7.48–7.39 (12 H, m, *PPh* 12,16-H), 7.35–7.26 (6 H, m, *PPh* 14-H), 7.10 (12 H, t,  $^3J_{HH}$  7.06, *PPh* 13,18-H), 6.81 (2 H, d,  $^3J_{HH}$  7.25, Acenap 3,8-H), 3.13 (4 H, s, 2 x  $CH_2$ );  $\delta_C$ (67.9 MHz;  $CDCl_3$ ; 25 °C;  $Me_4Si$ ) 143.2(s), 143.7(t, *J* 5.4), 130.0(s), 128.0 (t, *J* 5.2), 119.3(s), 30.1(s,  $CH_2$ );  $\delta_P$ (109 MHz,  $CDCl_3$ , 25 °C,  $H_3PO_4$ ) 20.2 ( $J_{PP}$  3020);  $\delta_{Se}$ (52 MHz,  $CDCl_3$ , 25 °C,  $PhSeSePh$ ) 167.3 (pt); [33]  $m/z$  ( $ES^+$ ) 874.00 ( $[M-SePh]^+$ , 100%).

**[Pt(PPh<sub>2</sub>Me)<sub>2</sub>L1] (3):** **3** was prepared following a similar procedure described for **1** but with Super Hydride (1.1 mL, 1.1 mmol), **L1** (0.12 g, 0.56 mmol) and *cis*-[PtCl<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub>] (0.375 g, 0.564 mmol). The resulting micro-crystalline solid was collected by filtration and washed with diethyl ether to yield the product as a bright orange powder (0.3 g, 65%); mp 275–278 °C; (Found: C, 55.9; H, 3.8. *Anal. Calc.* for  $C_{38}H_{34}PtP_2S_2$ : C, 56.2; H, 4.2%);  $\delta_H$ (400 MHz,  $CDCl_3$ , 25 °C,  $Me_4Si$ ) 7.46 (2 H, d,  $^2J_{HH}$  7.3, Acenap 4,7-H), 7.42–7.32 (8 H, m, *PPh* 12,16-H), 7.32–7.24 (8 H, m, *PPh* 13,18-H), 7.17 (4 H, d,  $^2J_{HH}$  7.3, *PPh* 14-H), 6.85 (2 H, d,  $^2J_{HH}$  7.2, Acenap 3,8-H), 3.06 (4 H, s, Acenap  $CH_2$ ), 1.84–1.70 (6 H, m,  $PCH_3$ );  $\delta_C$ (67.9 MHz;  $CDCl_3$ ; 25 °C;  $Me_4Si$ ) 141.9(s), 132.8(t, *J* 5.5, Ph-2), 131.4(s), 130.4(s), 128.3(t, *J* 5.2), 120.4(s), 119.5(s), 30.3(s), 15–14.4(m,  $CH_3$ );  $\delta_P$ (109 MHz,  $CDCl_3$ , 25 °C,  $H_3PO_4$ ) 4.51 ( $J_{PP}$  2926);  $m/z$  ( $ES^+$ ) 703.69 ( $[M-SPh]^+$ , 100%).

**[Pt(PPh<sub>2</sub>Me)<sub>2</sub>L2] (4):** **4** was prepared following a similar procedure described for **1** but with Super Hydride (1.1 mL, 1.1 mmol), **L2** (0.18 g, 0.56 mmol) and *cis*-[PtCl<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub>] (0.38 g, 0.56 mmol). The resulting micro-crystalline solid was collected by filtration and washed with diethyl ether to yield the product as a orange powder (0.2 g, 43%); mp 184–185 °C; (Found: C, 50.3; H, 3.7. *Anal. Calc.* for  $C_{38}H_{34}PtP_2Se_2$ : C, 50.3; H, 3.8%);  $\delta_H$ (400 MHz,  $CDCl_3$ , 25 °C,  $Me_4Si$ ) 7.82 (2 H, d,  $^3J_{HH}$  7.3, Acenap 4,7-H), 7.55–7.45 (9 H, m, *PPh* 14-H), 7.45–7.35 (4 H, m, *PPh* 12,16-H), 7.33–7.27 (8 H, m, *PPh* 13,18-H), 6.92 (2 H, d,  $^3J_{HH}$  7.2, Acenap 3,8-H), 3.18 (4 H, s, Acenap  $CH_2$ ), 1.91 (6 H, s,  $PCH_3$ );  $\delta_C$ (67.9 MHz;  $CDCl_3$ ; 25 °C;  $Me_4Si$ ) 143.4(s), 133.00–132.6(m), 130.4 (s), 128.2(t, *J* 5.1), 119.3(s), 30.1(s), 14.9–14.7(m,  $CH_3$ );  $\delta_P$ (162 MHz,  $CDCl_3$ , 25 °C,  $H_3PO_4$ ) 1.22 ( $J_{PP}$  2958);  $m/z$  ( $ES^+$ ) 929.07 ( $[M+Na]^+$ , 35%).

**[Pt(PPhMe)<sub>2</sub>L1] (5):** **5** was prepared following a similar procedure described for **1** but with Super Hydride (1.1 mL, 1.1 mmol), **L1** (0.12 g, 0.56 mmol) and *cis*-[PtCl<sub>2</sub>(PPhMe)<sub>2</sub>] (0.31 g, 0.56 mmol). The resulting micro-crystalline solid was collected by filtration and washed with diethyl ether to yield the product as a yellow solid (0.2, 50%); mp 265–270 °C; (Found: C, 48.8; H, 4.3. *Anal. Calc.* for  $C_{28}H_{30}PtP_2S_2$ : C, 48.9; H, 4.4%);  $\nu_{max}$  (KBr disk)/cm<sup>-1</sup>: 3442s, 3002w, 2908w, 2830w, 1627w, 1550w, 1479w, 1429s, 1402s, 1323w, 1293w, 1228w, 1178w, 1104w, 1033w, 947s, 906vs, 835w, 737w, 714w, 690w, 619w, 524w, 495w, 436w;  $\delta_H$ (400 MHz,  $CDCl_3$ , 25 °C,  $Me_4Si$ ) 7.78 (2 H, d,  $^3J_{HH}$  7.3, Acenap 4,7-H), 7.49–7.25 (8 H, m, *PPh* 12,16-H), 7.28 (2 H, d,  $^2J$  4.4, *PPh* 13,18-H), 6.99 (2 H, d,  $^3J_{HH}$  7.2, Acenap 3,8-H), 3.19 (4 H, s, Acenap  $CH_2$ ), 1.80–1.65 (6 H, m,  $PCH_3$ );  $\delta_C$ (67.9 MHz;  $CDCl_3$ ; 25 °C;  $Me_4Si$ ) 141.7(s), 140.7(s), 132.4(s), 132.2(s), 130.9(t, *J* 5.2), 130.3(s), 128.5(t, *J* 5.1), 127.7(t, *J* 6.7), 119.4(s), 30.5(s), 13.9–13.0(m,  $CH_3$ );  $\delta_P$ (109 MHz,  $CDCl_3$ , 25 °C,  $H_3PO_4$ ) -13.14 ( $J_{PP}$  2861,  $J_{PP}$  8.4);  $m/z$  ( $ES^+$ ) 578.70 ( $[M-SPh]^+$ , 100%).

**[Pt(PPhMe)<sub>2</sub>L2] (6):** **6** was prepared following a similar procedure described for **1** but with Super Hydride (1.1 mL, 1.1 mmol), **L2** (0.18 g, 0.56 mmol) and *cis*-[PtCl<sub>2</sub>(PPhMe)<sub>2</sub>] (0.31 g, 0.56 mmol). The resulting micro-crystalline solid was collected by filtration and washed with diethyl ether to yield a yellow solid (0.2 g, 45%); mp 184–185 °C;

(Found: C, 42.8; H, 3.2. *Anal. Calc.* for  $C_{28}H_{30}PtP_2Se_2$ : C, 43.0; H, 3.9%);  $\delta_H$ (400 MHz,  $CDCl_3$ , 25 °C,  $Me_4Si$ ) 7.88 (2 H, d,  $^3J_{HH}$  7.2, Acenap 4,7-H), 7.45–7.35 (4 H, m, *PPh* 12,16-H), 7.30–7.26 (4 H, m, *PPh* 13,18-H), 7.20 (2 H, m, 4-H), 6.85 (2 H, d,  $^3J_{HH}$  7.3, Acenap 3,8-H), 3.09 (4 H, s,  $CH_2$ ), 1.80–1.60 (12 H, m,  $PCH_3$ );  $\delta_C$ (67.9 MHz;  $CDCl_3$ ; 25 °C;  $Me_4Si$ ) 141.7(s), 140.7(s), 132.4(s), 132.2(s), 130.8(t, *J* 5.2), 130.3(s), 128.5(t, *J* 5.1), 127.6(t, *J* 6.7), 119.4(s), 30.5(s), 13.8–13.7(m,  $CH_3$ );  $\delta_P$ (109 MHz,  $CDCl_3$ , 25 °C,  $H_3PO_4$ ) -16.22 ( $J_{PP}$  2895,  $J_{PA-Se}$  67,  $J_{PA'-Se}$  40,  $J_{PP}$  12.4);  $\delta_{Se}$ (52 MHz,  $CDCl_3$ , 25 °C,  $PhSeSePh$ ) 426.2(pt); [33]  $m/z$  ( $ES^+$ ) 625.99 ( $[M-SePh]^+$ , 100%).

## Crystal Structure Analyses

X-ray crystal structures for **L1**, **L2**, and **6** were determined at -148(1) °C on the St Andrews Robotic Diffractometer [34] a Rigaku ACTOR-SM, Saturn 724 CCD area detector with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The data was corrected for Lorentz, polarisation and absorption. Data for compounds **1** and **2** were collected at -180(1) °C by using a Rigaku MM007 High brilliance RA generator (Mo K $\alpha$  radiation, confocal optic) and Saturn CCD system. At least a full hemisphere of data was collected using  $\omega$  scans. Intensities were corrected for Lorentz, polarisation and absorption. Data for compound **5** were collected at -148(1) °C on a Rigaku SCXmini CCD area detector with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The data were corrected for Lorentz, polarisation and absorption. The data for the complexes analysed was collected and processed using CrystalClear (Rigaku). [35] The structures were solved by direct methods [36] and expanded using Fourier techniques. [37] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure [38] crystallographic software package except for refinement, which was performed using SHELXL-97. [39] These X-ray data can be obtained free of charge via [www.ccdc.cam.ac.uk/contents/retrieving.html](http://www.ccdc.cam.ac.uk/contents/retrieving.html) or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) CCDC Nos: .

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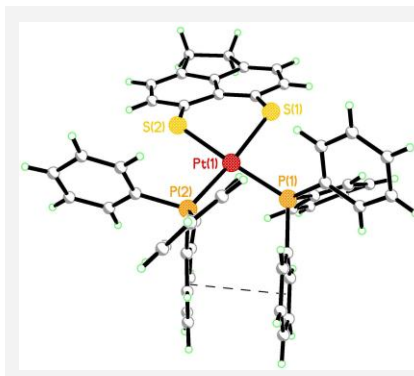
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## Entry for the Table of Contents ((Please choose one layout.))

### Layout 1:

((Six platinum bisphosphine complexes bearing 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dichalcogenoles AcenapE<sub>2</sub> E = S, Se, have been prepared, formed from metathetical addition of the dilithium precursors to *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] (R<sub>3</sub> = Ph<sub>3</sub>, Ph<sub>2</sub>Me, PhMe<sub>2</sub>).))



((Key Topic))

((Callum G. M. Benson, Catherine M. Schofield, Rebecca A. M. Randall, Lucy Wakefield, Fergus R. Knight, Alexandra M. Z. Slawin and J. Derek Woollins\*)) ..... Page No. – Page No.

((Platinum Complexes of 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dichalcogenoles))

**Keywords:** ((Chalcogen / Metathesis /

### Layout 2:

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((Key Topic))

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((Title))

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**Keywords:** ((Keyword 1 / Keyword 2 / Keyword 3 / Keyword 4 / Keyword 5))

## Supporting Information ((optional))

### Experimental Section

All experiments were carried out under an oxygen- and moisture-free nitrogen atmosphere using standard Schlenk techniques and glassware. Reagents were obtained from commercial sources and used as received. Dry solvents were collected from a MBraun solvent system. Elemental analyses were performed by Stephen Boyer at the London Metropolitan University. Infra-red spectra were recorded as KBr discs in the range 4000-300  $\text{cm}^{-1}$  on a Perkin-Elmer System 2000 Fourier transform spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with  $\delta(\text{H})$  and  $\delta(\text{C})$  referenced to external tetramethylsilane.  $^{31}\text{P}$  and  $^{77}\text{Se}$  NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with  $\delta(\text{P})$  and  $\delta(\text{Se})$  referenced to external phosphoric acid and dimethylselenide respectively. Assignments of  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra were made with the help of H-H COSY and HSQC experiments. All measurements were performed at 25 °C. All values reported for NMR spectroscopy are in parts per million (ppm). Coupling constants ( $J$ ) are given in Hertz (Hz). Mass spectrometry was performed by the University of St. Andrews Mass Spectrometry Service; Electrospray Mass Spectrometry (ESMS) was carried out on a Micromass LCT orthogonal accelerator time of flight mass spectrometer. Platinum metal precursors *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] (R<sub>3</sub> = Ph<sub>3</sub>, Ph<sub>2</sub>Me, PhMe<sub>2</sub>) were prepared following standard literature procedures.[12]

**5,6-dihydroacenaphtho[5,6-*cd*][1,2]dithiole [AcenapS<sub>2</sub>] (L1):** The title compound was prepared by a method previously described.[23] To a stirred solution of 5,6-dibromoacenaphthene (5.0 g, 16.03 mmol) and TMEDA (4.8 mL, 16.03 mmol) in diethyl ether (200 mL) was slowly added a 2.5 M hexane solution of *n*-butyllithium (6.4 mL, 16.03 mmol) at -78 °C. After the mixture was stirred for 15 min at this temperature, sulfur flowers (0.51 g, 16.03 mmol) were added and stirring was continued at -40 °C for 2 h. The mixture was cooled again to -78 °C, after which a 2.5 M hexane solution of *n*-butyllithium (6.4 mL, 16.03 mmol) was added and the reaction mixture stirred at this temperature for 15 min. Additional sulfur (0.51 g, 16.03 mmol) was added and the reaction mixture stirred for a further 2 h at -40 °C. The mixture was then quenched with acetic acid (2 mL) and exposed to an air stream overnight for oxidation. The resulting solution was concentrated under reduced pressure and after water was added, the mixture was extracted with dichloromethane. The extract was dried over anhydrous magnesium sulfate. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (hexane). An analytically pure sample was obtained by recrystallization from hexane to give the desired product as orange crystals (0.70 g, 20%); mp 178-182 °C; (Found: C, 66.5; H, 3.8. *Anal. Calc.* for C<sub>12</sub>H<sub>8</sub>S<sub>2</sub>: C, 66.6; H, 3.7%);  $\nu_{\text{max}}$ (KBr disk)/ $\text{cm}^{-1}$ : 3425s, 3040w, 2918s, 2833w, 2375w, 1825w, 1628w, 1596w, 1561s, 1511w, 1483w, 1450w, 1409s, 1394vs, 1390vs, 1321w, 1252w, 1226s, 1207s, 1141w, 1093w, 1052w, 1033s, 916w, 828vs, 801vs, 797vs, 749w, 719w, 692w, 606s, 546w, 527w, 459w, 383w, 305s;  $\delta_{\text{H}}$ (270 MHz, CDCl<sub>3</sub>, 25 °C, Me<sub>4</sub>Si) 7.06 (1 H, d,  $^3J_{\text{HH}}$  7.5, Acenap 4,7-H), 7.02 (1 H, d,  $^3J_{\text{HH}}$  7.2, Acenap 3,8-H), 3.29 (4 H, s, 2 x CH<sub>2</sub>);  $\delta_{\text{C}}$ (67.9 MHz; CDCl<sub>3</sub>; 25 °C; Me<sub>4</sub>Si) 121.1(s), 116.9(s), 30.7(s, CH<sub>2</sub>);  $m/z$  (ES<sup>+</sup>) 215.87 ([M]<sup>+</sup>, 100%).

**5,6-dihydroacenaphtho[5,6-*cd*][1,2]diselenole [AcenapSe<sub>2</sub>] (L2):** The title compound was prepared by a method previously described.[23] To a stirred solution of 5,6-dibromoacenaphthene (2.62 g, 8.40 mmol) and TMEDA (2.5 mL, 16.1 mmol) in diethyl ether (200 mL) was slowly added a 2.5 M hexane solution of *n*-butyllithium (3.4 mL, 8.40 mmol) at -78 °C. After the mixture was stirred for 15 min at this temperature, selenium powder (0.66 g, 8.40 mmol) was added and stirring was continued at -40 °C for 2 h. The mixture was cooled again to -78 °C, after which a 2.5 M hexane solution of *n*-butyllithium (3.4 mL, 8.40 mmol) was added and the reaction mixture stirred at this temperature for 15 min. Additional selenium powder (0.66 g, 8.40 mmol) was added and the reaction mixture stirred for a further 2 h at -40 °C. The mixture was then quenched with acetic acid (2 mL) and exposed to an air stream overnight for oxidation. The resulting solution was concentrated under reduced pressure and after water was added, the mixture was extracted with dichloromethane. The extract was dried over anhydrous magnesium sulfate. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (hexane/dichloromethane). An analytically pure sample was obtained by recrystallization from boiling toluene to give the desired product as green crystals (0.83 g, 32%); mp 198-200 °C; (Found: C, 46.5; H, 2.6. *Anal. Calc.* for C<sub>12</sub>H<sub>8</sub>Se<sub>2</sub>: C, 46.5; H, 2.6%);  $\nu_{\text{max}}$ (KBr disk)/ $\text{cm}^{-1}$ : 2914s, 2829w, 1829w, 1564 vs, 1479w, 1445w, 1415vs, 1405vs, 1377vs, 1322s, 1251w, 1225s, 1093w, 1043w, 1019s, 913w, 830vs, 799vs, 745s, 728s, 700s, 600s, 496s, 463w;  $\delta_{\text{H}}$ (270 MHz, CDCl<sub>3</sub>, 25 °C, Me<sub>4</sub>Si) 7.21 (1 H, d,  $^3J_{\text{HH}}$  7.4 Hz, Acenap 4,7-H), 7.05 (1 H, d,  $^3J_{\text{HH}}$  7.2 Hz, Acenap 3,8-H), 3.26 (4 H, s, 2 x CH<sub>2</sub>);  $\delta_{\text{C}}$ (67.9 MHz; CDCl<sub>3</sub>; 25 °C; Me<sub>4</sub>Si) 121.7(s), 121.2(s), 30.4(s, Acenap CH<sub>2</sub>);  $\delta_{\text{Se}}$ (51.5 MHz; CDCl<sub>3</sub>; 25 °C; Me<sub>2</sub>Se) 424(s);  $m/z$  (ES<sup>+</sup>) 311.90([M+H]<sup>+</sup>, 100%), 309.91 ([M]<sup>+</sup>, 70%).

**[Pt(PPh<sub>3</sub>)<sub>2</sub>L1] (1):** Super Hydride (1.1 mL of a 1.0 M solution in THF, 1.1 mmol) was added in one portion to a solution of 5,6-dihydroacenaphtho[5,6-*cd*][1,2]dithiole (AcenapS<sub>2</sub>) L1 (0.12 g, 0.56 mmol) in THF (20 mL). A colour change from bright red to pale yellow was observed, along with a small evolution of gas. The solution was transferred using a syringe to a suspension of *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.45 g, 0.56 mmol) in THF (10 mL) and stirred for 2 days giving a yellow solution. The mixture was filtered through a silica pad and eluted with dichloromethane (100 mL). The filtrate was evaporated to dryness under reduced pressure and re-dissolved in a minimum amount of dichloromethane (~10 mL). Diethyl ether (25 mL) and hexane (50 mL) were added slowly to induce precipitation. The resulting micro-crystalline solid was collected by filtration and washed with diethyl ether to yield the product as a light orange powder (0.4 g, 74%); mp 282-284 °C; (Found: C, 61.4; H,

4.0. *Anal. Calc.* for  $C_{48}H_{38}P_2PtS_2$ : C, 61.6; H, 4.1%;  $\nu_{max}$ (KBr disk)/ $cm^{-1}$ : 3668s, 3286w, 2972w, 2894w, 2355w, 1863w, 1694w, 1603w, 1508w, 1565w, 1503w, 1447vs, 1421s, 1391w, 1320w, 1296w, 1237w, 1203w, 1170w, 1113s, 1079s, 1011w, 980w, 863w, 768w, 714vs, 675vs, 552vs, 531vs, 502s, 485s, 404w, 281s;  $\delta_H$ (400 MHz,  $CDCl_3$ , 25 °C,  $Me_4Si$ ) 7.48-7.38 (12 H, m, *PPh* 12,16-H), 7.34-7.26 (6 H, m, *PPh* 14-H), 7.27 (2 H, d,  $^3J_{HH}$  7.3, Acenap 4,7-H), 7.14 (12 H, td,  $^3J_{HH}$  7.7,  $^4J_{HH}$  1.8, *PPh* 13,18-H), 6.90 (2 H, d,  $^3J_{HH}$  7.3, Acenap 3,8-H), 3.17 (4 H, s, Acenap- $CH_2$ );  $\delta_C$ (75 MHz,  $CDCl_3$ , 25 °C,  $Me_4Si$ ) 142.0(s), 140.7(s), 135.4-134.8 (m), 130.4 (s), 128.6-127.4 (m), 119.7(s), 30.9(s,  $CH_2$ );  $\delta_P$ (109 MHz,  $CDCl_3$ , 25 °C,  $H_3PO_4$ ) 23.5 ( $J_{PPt}$  2980); m/z ( $ES^+$ ) 826.66 ( $[M-SPh]^+$ , 100%).

**[Pt( $PPh_3$ ) $_2$ L2] (2):** Super Hydride (1.1 mL of a 1.0 M solution in THF, 1.1 mmol) was added in one portion to a solution of 5,6-dihydroacenaptho[5,6-*cd*][1,2]diselenole (AcenapSe $_2$ ) **L2** (0.18 g, 0.56 mmol) in THF (20 mL). A colour change from bright red to pale yellow was observed, along with a small evolution of gas. The solution was transferred using a syringe to a suspension of *cis*-[PtCl $_2$ ( $PPh_3$ ) $_2$ ] (0.45 g, 0.56 mmol) in THF (10 mL) and stirred for 2 days giving a yellow solution. The mixture was filtered through a silica pad and eluted with dichloromethane (100 mL). The filtrate was evaporated to dryness under reduced pressure and re-dissolved in a minimum amount of dichloromethane (~10 mL). Diethyl ether (25 mL) and hexane (50 mL) were added slowly to induce precipitation. The resulting solid was filtered off and washed with toluene (5 mL) and diethyl ether (2x10 mL) and dried *in vacuo* to yield an orange powder (0.3 g, 54%); mp 185-186 °C; (Found: C, 55.9; H, 3.8. *Anal. Calc.* for  $C_{48}H_{38}PtP_2Se_2$ : C, 56.0; H, 3.7%;  $\nu_{max}$ (KBr disk)/ $cm^{-1}$ : 3237w, 2746w, 1997w, 1858w, 1767w, 1694w, 1606w, 1562w, 1494s, 1446vs, 1419s, 1395w, 1349w, 1288w, 1236w, 1201s, 1172w, 1110vs, 1077vs, 1008w, 939s, 884s, 826w, 765s, 721vs, 667vs, 551vs, 530vs, 501s, 480vs, 404w;  $\delta_H$ (400 MHz,  $CDCl_3$ , 25 °C,  $Me_4Si$ ) 7.51 (2 H, d,  $^3J_{HH}$  7.28, Acenap 4,7-H), 7.48-7.39 (12 H, m, *PPh* 12,16-H), 7.35-7.26 (6 H, m, *PPh* 14-H), 7.10 (12 H, t,  $^3J_{HH}$  7.06, *PPh* 13,18-H), 6.81 (2 H, d,  $^3J_{HH}$  7.25, Acenap 3,8-H), 3.13 (4 H, s, 2 x  $CH_2$ );  $\delta_C$ (67.9 MHz;  $CDCl_3$ ; 25 °C;  $Me_4Si$ ) 143.2(s), 143.7(t,  $J$  5.4), 130.0(s), 128.0 (t,  $J$  5.2), 119.3(s), 30.1(s,  $CH_2$ );  $\delta_P$ (109 MHz,  $CDCl_3$ , 25 °C,  $H_3PO_4$ ) 20.2 ( $J_{PPt}$  3020);  $\delta_{Se}$ (52 MHz,  $CDCl_3$ , 25 °C,  $PhSeSePh$ ) 167.3 (pt); m/z ( $ES^+$ ) 874.00 ( $[M-SePh]^+$ , 100%).

**[Pt( $PPh_2Me$ ) $_2$ L1] (3):** Super Hydride (1.1 mL of a 1.0 M solution in THF, 1.1 mmol) was added in one portion to a solution of (AcenapSe $_2$ ) **L1** (0.12 g, 0.56 mmol) in THF (20 mL). A colour change from bright red to pale yellow was observed, along with a small evolution of gas. The solution was transferred using a syringe to a suspension of *cis*-[PtCl $_2$ ( $PPh_2Me$ ) $_2$ ] (0.375 g, 0.564 mmol) in THF (10 mL) and stirred for 2 days giving a yellow solution. The mixture was filtered through a silica pad and eluted with dichloromethane (100 mL). The filtrate was evaporated to dryness under reduced pressure and re-dissolved in a minimum amount of dichloromethane (~10 mL). Diethyl ether (25 mL) and hexane (50 mL) were added slowly to induce precipitation. The resulting micro-crystalline solid was collected by filtration and washed with diethyl ether to yield the product as a bright orange powder (0.3 g, 65%); mp 275-278 °C; (Found: C, 55.9; H, 3.8. *Anal. Calc.* for  $C_{38}H_{34}PtP_2S_2$ : C, 56.2; H, 4.2%;  $\nu_{max}$ (KBr disk)/ $cm^{-1}$ : 3421vs, 3051w, 2920w, 2670w, 1638w, 1592w, 1483w, 1435s, 1405w, 1353w, 1287w, 1228w, 1184w, 1103s, 1024w, 994w, 890vs, 841w, 739s, 693vs, 619w, 513s, 452w, 326w;  $\delta_H$ (400 MHz,  $CDCl_3$ , 25 °C,  $Me_4Si$ ) 7.46 (2 H, d,  $^2J_{HH}$  7.3, Acenap 4,7-H), 7.42-7.32 (8 H, m, *PPh* 12,16-H), 7.32-7.24 (8 H, m, *PPh* 13,18-H), 7.17 (4 H, d,  $^2J_{HH}$  7.3, *PPh* 14-H), 6.85 (2 H, d,  $^2J_{HH}$  7.2, Acenap 3,8-H), 3.06 (4 H, s, Acenap  $CH_2$ ), 1.84-1.70 (6 H, m,  $PCH_3$ );  $\delta_C$ (67.9 MHz;  $CDCl_3$ ; 25 °C;  $Me_4Si$ ) 141.9(s), 132.8(t,  $J$  5.5,  $Ph$ -2), 131.4(s), 130.4(s), 128.3(t,  $J$  5.2), 120.4(s), 119.5(s), 30.3(s), 15-14.4(m,  $CH_3$ );  $\delta_P$ (109 MHz,  $CDCl_3$ , 25 °C,  $H_3PO_4$ ) 4.51 ( $J_{PPt}$  2926); m/z ( $ES^+$ ) 703.69 ( $[M-SPh]^+$ , 100%).

**[Pt( $PPh_2Me$ ) $_2$ L2] (4):** Super Hydride (1.1 mL of a 1.0 M solution in THF, 1.1 mmol) was added in one portion to a solution of (AcenapSe $_2$ ) **L2** (0.18 g, 0.56 mmol) in THF (20 mL). A colour change from bright red to pale yellow was observed, along with a small evolution of gas. The solution was transferred using a syringe to a suspension of *cis*-[PtCl $_2$ ( $PPh_2Me$ ) $_2$ ] (0.38 g, 0.56 mmol) in THF (10 mL) and stirred for 2 days giving a yellow solution. The mixture was filtered through a silica pad and eluted with dichloromethane (100 mL). The filtrate was evaporated to dryness under reduced pressure and re-dissolved in a minimum amount of dichloromethane (~10 mL). Diethyl ether (25 mL) and hexane (50 mL) were added slowly to induce precipitation. The resulting micro-crystalline solid was collected by filtration and washed with diethyl ether to yield the product as a orange powder (0.2 g, 43%); mp 184-185 °C; (Found: C, 50.3; H, 3.7. *Anal. Calc.* for  $C_{38}H_{34}PtP_2Se_2$ : C, 50.3; H, 3.8%;  $\nu_{max}$ (KBr disk)/ $cm^{-1}$ : 3425s, 3053w, 2922w, 2844w, 1632w, 1479w, 1434vs, 1401w, 1332w, 1305w, 1279w, 1255w, 1186w, 1159w, 1099vs, 1024w, 1000w, 884vs, 836w, 806w, 734s, 689s, 608w, 507s, 447w, 333w;  $\delta_H$ (400 MHz,  $CDCl_3$ , 25 °C,  $Me_4Si$ ) 7.82 (2 H, d,  $^3J_{HH}$  7.3, Acenap 4,7-H), 7.55-7.45 (9 H, m, *PPh* 14-H), 7.45-7.35 (4 H, m, *PPh* 12,16-H), 7.33-7.27 (8 H, m, *PPh* 13,18-H), 6.92 (2 H, d,  $^3J_{HH}$  7.2, Acenap 3,8-H), 3.18 (4 H, s, Acenap  $CH_2$ ), 1.91 (6 H, s,  $PCH_3$ );  $\delta_C$ (67.9 MHz;  $CDCl_3$ ; 25 °C;  $Me_4Si$ ) 143.4(s), 133.00-132.6(m), 130.4 (s), 128.2(t,  $J$  5.1), 119.3(s), 30.1(s), 14.9-14.7(m,  $CH_3$ );  $\delta_P$ (162 MHz,  $CDCl_3$ , 25 °C,  $H_3PO_4$ ) 1.22 ( $J_{PPt}$  2958); m/z ( $ES^+$ ) 929.07 ( $[M+Na]^+$ , 35%).

**[Pt( $PPhMe_2$ ) $_2$ L1] (5):** Super Hydride (1.1 mL of a 1.0 M solution in THF, 1.1 mmol) was added in one portion to a solution of (AcenapSe $_2$ ) **L1** (0.12 g, 0.56 mmol) in THF (20 mL). A colour change from bright red to pale yellow was observed, along with a small evolution of gas. The solution was transferred using a syringe to a suspension of *cis*-[PtCl $_2$ ( $PPhMe_2$ ) $_2$ ] (0.31 g, 0.56 mmol) in THF (10 mL) and stirred for 2 days giving a yellow solution. The mixture was filtered through a silica pad and eluted with dichloromethane (100 mL). The filtrate was evaporated to dryness under reduced pressure and re-dissolved in a minimum amount of dichloromethane (~10 mL). Diethyl ether (25 mL) and hexane (50 mL) were added slowly to induce precipitation. The resulting micro-crystalline solid was collected by filtration and washed with diethyl ether to yield the product as a yellow solid (0.2, 50%); mp 265-270 °C; (Found: C, 48.8; H, 4.3. *Anal. Calc.* for  $C_{28}H_{30}PtP_2S_2$ : C, 48.9; H, 4.4%;  $\nu_{max}$  (KBr disk)/ $cm^{-1}$ : 3442s, 3002w, 2908w, 2830w, 1627w, 1550w, 1479w, 1429s, 1402s, 1323w, 1293w, 1228w,



1178w, 1104w, 1033w, 947s, 906vs, 835w, 737w, 714w, 690w, 619w, 524w, 495w, 436w;  $\delta_{\text{H}}$ (400 MHz,  $\text{CDCl}_3$ , 25 °C,  $\text{Me}_4\text{Si}$ ) 7.78 (2 H, d,  $^3J_{\text{HH}}$  7.3, Acenap 4,7-H), 7.49-7.25 (8 H, m, *PPh* 12,16-H), 7.28 (2 H, d,  $^2J$  4.4, *PPh* 13,18-H), 6.99 (2 H, d,  $^3J_{\text{HH}}$  7.2, Acenap 3,8-H), 3.19 (4 H, s, Acenap  $\text{CH}_2$ ), 1.80-1.65 (6 H, m,  $\text{PCH}_3$ );  $\delta_{\text{C}}$ (67.9 MHz;  $\text{CDCl}_3$ ; 25 °C;  $\text{Me}_4\text{Si}$ ) 141.7(s), 140.7(s), 132.4(s), 132.2(s), 130.9(t,  $J$  5.2), 130.3(s), 128.5(t,  $J$  5.1), 127.7(t,  $J$  6.7), 119.4(s), 30.5(s), 13.9-13.0(m,  $\text{CH}_3$ );  $\delta_{\text{P}}$ (109 MHz,  $\text{CDCl}_3$ , 25 °C,  $\text{H}_3\text{PO}_4$ ) -13.14 ( $J_{\text{Pt}}$  2861,  $J_{\text{PP}}$  8.4);  $m/z$  ( $\text{ES}^+$ ) 578.70 ( $[\text{M-SPh}]^+$ , 100%).

**[Pt(PPhMe<sub>2</sub>)<sub>2</sub>L2] (6):** Super Hydride (1.1 mL of a 1.0 M solution in THF, 1.1 mmol) was added in one portion to a solution of (AcenapSe<sub>2</sub>) **L2** (0.18 g, 0.56 mmol) in THF (20 mL). A colour change from bright red to pale yellow was observed, along with a small evolution of gas. The solution was transferred using a syringe to a suspension of *cis*-[PtCl<sub>2</sub>(PPhMe<sub>2</sub>)] (0.31 g, 0.56 mmol) in THF (10 mL) and stirred for 2 days giving a yellow solution. The mixture was filtered through a silica pad and eluted with dichloromethane (100 mL). The filtrate was evaporated to dryness under reduced pressure and re-dissolved in a minimum amount of dichloromethane (~10 mL). Diethyl ether (25 mL) and hexane (50 mL) were added slowly to induce precipitation. The resulting micro-crystalline solid was collected by filtration and washed with diethyl ether to yield a yellow solid (0.2 g, 45%); mp 184-185 °C; (Found: C, 42.8; H, 3.2. *Anal. Calc.* for C<sub>28</sub>H<sub>30</sub>PtP<sub>2</sub>Se<sub>2</sub>: C, 43.0; H, 3.9%);  $\nu_{\text{max}}$  (KBr disk)/cm<sup>-1</sup>: 3439s, 3044w, 3008w, 2961w, 2917w, 2272w, 1549w, 1479w, 1433s, 1328w, 1228w, 1186w, 1106s, 949vs, 906vs, 841s, 745s, 716w, 690w, 496w, 441w;  $\delta_{\text{H}}$ (400 MHz,  $\text{CDCl}_3$ , 25 °C,  $\text{Me}_4\text{Si}$ ) 7.88 (2 H, d,  $^3J_{\text{HH}}$  7.2, Acenap 4,7-H), 7.45-7.35 (4 H, m, *PPh* 12,16-H), 7.30-7.26 (4 H, m, *PPh* 13,18-H), 7.20 (2 H, m, 4-H), 6.85 (2 H, d,  $^3J_{\text{HH}}$  7.3, Acenap 3,8-H), 3.09 (4 H, s,  $\text{CH}_2$ ), 1.80-1.60 (12 H, m,  $\text{PCH}_3$ );  $\delta_{\text{C}}$ (67.9 MHz;  $\text{CDCl}_3$ ; 25 °C;  $\text{Me}_4\text{Si}$ ) 141.7(s), 140.7(s), 132.4(s), 132.2(s), 130.8(t,  $J$  5.2), 130.3(s), 128.5(t,  $J$  5.1), 127.6(t,  $J$  6.7), 119.4(s), 30.5(s), 13.8-13.7(m,  $\text{CH}_3$ );  $\delta_{\text{P}}$ (109 MHz,  $\text{CDCl}_3$ , 25 °C,  $\text{H}_3\text{PO}_4$ ) -16.22 ( $J_{\text{Pt}}$  2895,  $J_{\text{PA-Se}}$  67,  $J_{\text{PA'-Se}}$  40,  $J_{\text{PP}}$  12.4);  $\delta_{\text{Se}}$ (52 MHz,  $\text{CDCl}_3$ , 25 °C, PhSeSePh) 426.2(pt);  $m/z$  ( $\text{ES}^+$ ) 625.99 ( $[\text{M-SePh}]^+$ , 100%).